

## IV.C.1k ORNL Progress within the DOE Center of Excellence for Hydrogen Sorption: Synthesis and Processing of Single-Walled Carbon Nanohorns for Hydrogen Storage and Catalyst Supports

David B. Geohegan (Primary Contact),  
Mina Yoon, Alex A. Puretzky,  
Christopher M. Rouleau, Norbert Thonnard,  
Gerd Duscher, and Karren More  
Oak Ridge National Laboratory  
Materials Science and Technology Division  
and the Center for Nanophase Materials Sciences  
1 Bethel Valley Road, MS-6056  
Oak Ridge, TN 37831  
Phone: (865) 576-5097; Fax: 865-574-1753  
E-mail: geohegandb@ornl.gov

DOE Technology Development Manager:  
Carole Read  
Phone: (202) 586-3152; Fax: (202) 586-9811  
E-mail: Carole.Read@ee.doe.gov

### Subcontractors:

- Oak Ridge Institute for Science and Education, Oak Ridge, TN
- University of Tennessee, Knoxville, TN

Project Start Date: 2005

Project End Date: Project continuation and direction determined annually by DOE

### Objectives

The overall objective of the project is to exploit the unique morphology, tunable porosity and excellent metal supportability of single-walled carbon nanohorns (SWNHs) to optimize hydrogen uptake and binding energy through an understanding of metal-carbon interactions and nanoscale confinement. Specifically, in the current year, the objectives are to:

- Develop activation processes to nanoengineer sub-nm pores in SWNHs with high binding energy.
- Develop new techniques to Ca-decorate opened SWNHs and test the theoretical predictions of enhanced uptake and smooth coatings.
- To address computationally hydrogen storage in metal-decorated carbons, such as Ca-O-SWNHs and other charged nanostructures, which are designed with high static electric fields in nanoengineered pores or layers.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (B) System Cost
- (C) Efficiency
- (D) Durability/Operability
- (J) Thermal Management
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

This project is developing nanoengineered metal-decorated SWNHs for use as effective hydrogen storage media to satisfy DOE system targets. The project is addressing the 2010 system targets of:

- System Gravimetric Capacity: 2 kWh/kg (0.06 kg H<sub>2</sub>/kg system)
- System Volumetric Capacity: 1.5 kWh/L (0.045 kg H<sub>2</sub>/L system)
- Charging/Discharging Rates: 3 min for 5 kg system fill

Currently, this project has demonstrated gravimetric hydrogen uptakes of SWNHs between 0.6-1.5 wt% at room temperature, ~ 3.5 wt% at 77 K, and ~6.4 wt% at 30 K. The volumetric capacity demonstrated to date is 35 g/L for compressed pellets of decorated, opened nanohorns which is 67% of the 2010 system target. This project also will address the high thermal conductivity requirements required for system charging through incorporation of high thermal diffusivity (2.1 cm<sup>2</sup>/s) porous aligned nanotube arrays with the nanohorn storage medium.

### Accomplishments

- High surface areas: SWNHs were synthesized in gram quantities with pore sizes adjusted to maximize surface area (2,142 m<sup>2</sup>/g) and increase excess storage (3.5 wt% at 77 K).
- Tunable, small pores: Nuclear magnetic resonance (NMR) confirmed the majority of storage in the

interstitial (~0.5 nm) pores on large SWNHs, and in activated pores (<1 nm) in short-SWNHs. These NMR shifts are the highest among all materials studied, indicating storage in very small pores. Work continues to understand the activation process, but is aided by the stability of the nanohorn aggregate structure which is defined at very high temperatures during synthesis.

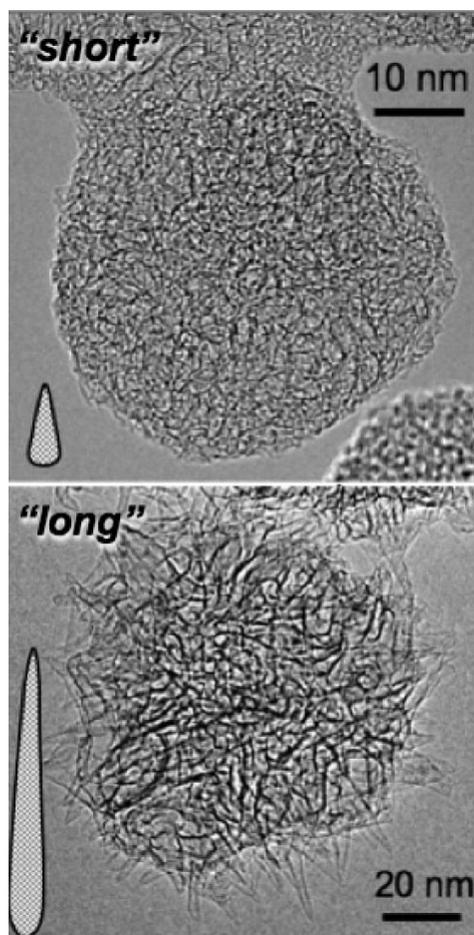
- Room temperature storage: Undecorated, short oxidized-SWNHs (o-SWNHs) reversibly store significant hydrogen (0.6 wt% at 30 bar) at room temperature, comparable to bridged metal-organic frameworks and Pt-decorated o-SWNHs (1.5 wt% at 100 bar). These “nanoengineered pores” are defined both by the unique nanostructure self-assembled during synthesis, and by the activated pores during oxidation.
- Enhanced Binding Due to Metal Decoration - Doping-Induced Charge Separation - Methods of vapor phase Ca-decoration were developed and found to result in smooth decoration unlike decoration by transition metals which results in small nanoparticles. These results confirm our theoretical predictions, which predict that of all the elements, alkaline earth metals Ca and Sr should have a special ability to coat C nanostructures without clustering while providing sufficient electric field strength to polarize and bind H<sub>2</sub> with 8.4 wt% and 0.4 eV for Ca.



## Introduction

SWNHs are carbon nanostructures with a unique morphology with potential for high capacity hydrogen storage media capable of satisfying DOE technical targets. Nanohorns are cone-shaped, atomic-layer-thick nanostructures which contain preferred hydrogen adsorption sites in their tips and have variable internal and interstitial pores that have been shown to contain hydrogen at liquid hydrogen density or higher (Figure 1). They can be functionalized by tailoring their pores and by metal decoration. They can be produced in large quantities, and have been shown to serve as excellent metal catalyst supports for fuel cells and batteries in addition to their potential as sorbents.

The ultimate goal of this project is to make use of SWNH complexes for efficient hydrogen storage media by (a) utilizing their high surface areas effectively to meet hydrogen gravimetric DOE targets, (b) optimizing their geometries for containing high volumetric densities of hydrogen, and (c) increasing their binding strength to hydrogen by metal decoration for ambient condition hydrogen storage application.



**FIGURE 1.** Aggregates of “short” and “long” single-wall carbon nanohorn aggregates produced by laser vaporization. Schematic representation of individual nanohorns shown.

## Approach

Carbon nanohorn aggregates are assembled from the “bottom up” from individual nanohorns. Our approach is threefold. First, the shape of individual nanohorns is tuned during synthesis to find morphologies with adsorption sites and high binding energies (e.g., in the tips of SWNHs). Second, the nanohorn aggregates have innate interstitial pores which can be tuned by oxidative treatments and other processing techniques (heat, compression, etc.). The internal pores and external pores can be investigated separately. Thus, the nanospaces of the pure carbon framework can be engineered to understand and optimize hydrogen storage in these “bottom up” assembled, pure-carbon structures. Third, metals are used to coat or decorate the activated aggregates to explore spillover based storage or store hydrogen directly on the metal coating. This overall approach permits the storage due to engineered nanospaces and that resulting from metals to be explored and tuned separately.

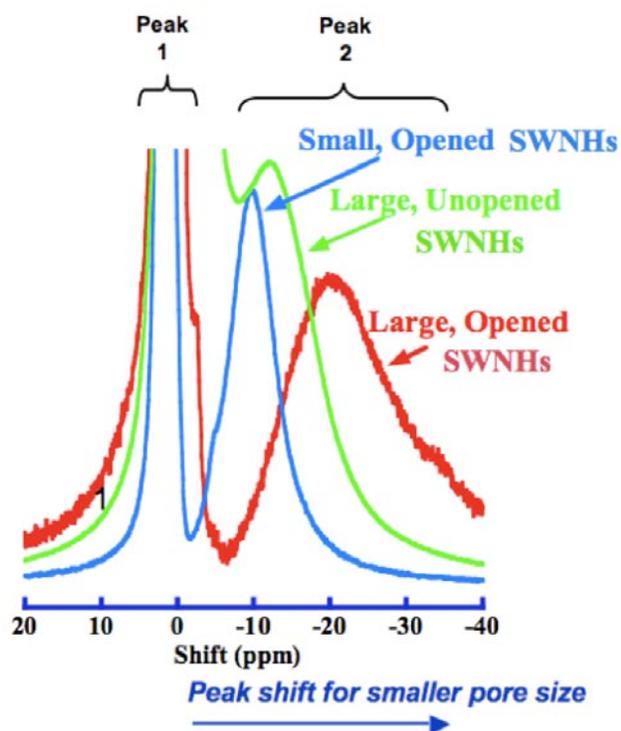
## Results

The morphology of the SWNHs was adjusted by tuning the pulse width and energy of the laser used in the carbon vaporization process, producing “large” and “small” carbon nanohorns as shown in Figure 1. The pores responsible for the majority of hydrogen storage in these as-produced and activated (‘opened’) aggregates were compared using an NMR technique by Hydrogen Sorption Center of Excellence partners at the University of North Carolina. The results (Figure 2) revealed that aggregates of ‘large’ nanohorns possess interstitial pores which store significant quantities of hydrogen in sub-nm pores (where small SWNHs do not). The internal and slit pores of the small SWNHs, revealed after oxidation, are the favored sites for hydrogen storage. These results indicate that interstitial pores provide more opportunity as preferred sites for hydrogen storage than previously recognized, and that synthesis conditions should be tuned to optimize the pore volume in these sites.

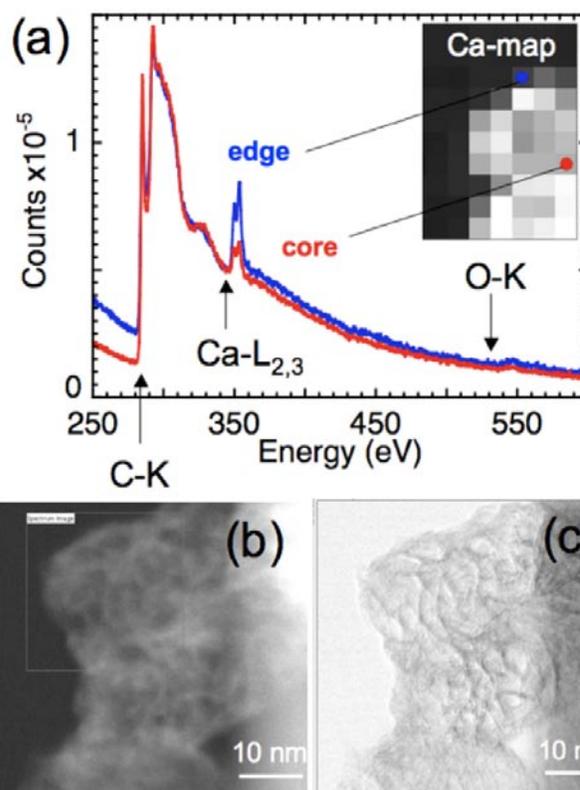
Efforts on metal decoration of the activated SWNHs concentrated upon processing techniques to attempt Ca decoration. Several processing techniques were implemented to decorate SWNHs with Ca. These included in situ vaporization of Ca during SWNH

synthesis, vaporization of C into Ca vapor, and post-synthesis infiltration of Ca vapor at high temperatures. The latter technique proved successful. High resolution transmission electron microscopy and Z-contrast scanning transmission electron microscopy/electron energy loss spectroscopy (EELS) measurements (Figure 3) were performed to understand whether Ca formed smooth, uniform coatings as predicted by theory. As shown in Figures 3(b) and 3(c), Ca was uniformly distributed within and on the outer surfaces of opened, small SWNHs. EELS measurements confirm that the controlled atmosphere processing utilized in the coating process resulted in insignificant oxidation of the Ca.

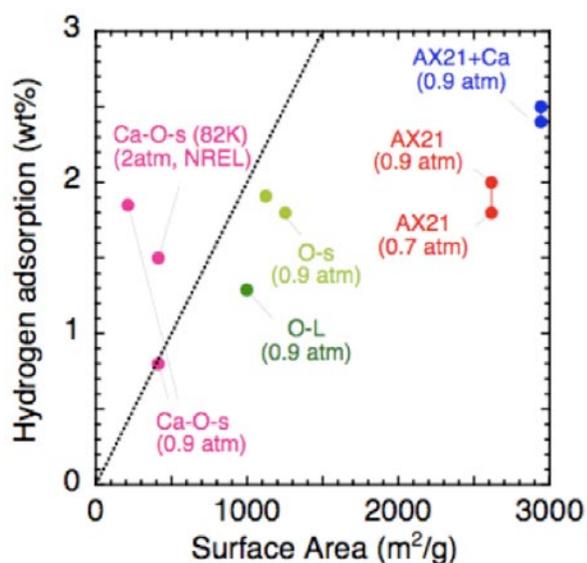
Nitrogen surface area measurements of the Ca-coated SWNHs, however, indicated that the Ca coating resulted in a major reduction in surface area (from  $\sim 1,200$   $\text{m}^2/\text{g}$  to  $\sim 300$   $\text{m}^2/\text{g}$ ) as shown in Figure 4. Since the infiltration process did not have in situ process control during these experiments, significant coating and pore blocking could be expected. Hydrogen adsorption isotherm measurements were performed at 77 K and 0.9 atm to compare the Ca-decorated o-SWNHs with the undecorated o-SWNHs. The isotherms were reversible,



**FIGURE 2.** NMR measurements (University of North Carolina) revealing the hydrogen stored in sub-nm pores in large and small nanohorns, opened and unopened by oxidation. The shift of peak 2 is greater for smaller diameter pores. The interstitial pores in large nanohorns surprisingly store hydrogen in smaller pores than the internal pores of small nanohorns.



**FIGURE 3.** Electron energy loss spectra of Ca-decorated SWNHs, showing Ca, lack of O, and map of Ca in an aggregate shown in (b) Z-contrast scanning transmission electron microscopy, high-angle annular dark-field image and (c) scanning transmission electron microscopy bright field image. The Ca appears uniformly distributed in the SWNH aggregate. (G. Duscher, University of Tennessee.)



**FIGURE 4.** Comparison of hydrogen adsorption measurements at low (0.7 – 2 atm.) pressure and 77 K vs. surface area. The Ca-decorated samples exhibit a higher figure of merit despite greatly reduced surface area.

and the Ca-decorated o-SWNHs isotherms indicated possible capillary condensation. To account for the difference in surface areas between the different samples, a figure of merit was defined as the wt% hydrogen measured per atmosphere hydrogen gas divided by 500 m<sup>2</sup>/g. Typically at high pressures, high surface area activated carbons often exhibit 1 wt% excess adsorption at 77 K for every 500 m<sup>2</sup>/g surface area (line in Figure 4, usually obtained at pressures >20 bar). However it is evident that the Ca-decorated o-SWNHs outperform undecorated samples and exceed this metric even at low (~1 bar) pressures, with a figure of merit a factor of 4 higher.

Preliminary measurements on Ca-decorated activated carbons (e.g., AX-21 obtained from Caltech) were performed to extend these measurements to commercial nanocarbons, however the coatings and modest improvements demonstrated are preliminary and will be pursued further.

## Conclusions and Future Directions

This project has demonstrated that pore sizes in pure carbon nanohorn aggregates can be tuned 1) during synthesis, and 2) during activation, and that this sometimes results in room temperature binding of up to 1.5 wt% hydrogen. The effects of metal decoration have been demonstrated. Enhanced storage at room temperature in Pt- and Pd-decorated SWNHs were investigated by neutron scattering, and indicate that spillover may be partly responsible. However, metal decoration with Ca has been shown to result in smooth

nanoparticle-free coatings and anomalously high storage, in agreement with our proposed mechanism of *polarization induced by high local electric fields* resulting from the alkaline-earth metal “doping” of C by decoration.

Future work should pursue this highly promising new direction on two fronts. First, work should continue with high-surface area carbons to maintain high surface areas while uniformly coating these materials. For nanohorns the Ca-coating process can be optimized by integrating it as an inherent part of the synthesis process, while for activated carbons in situ process monitoring during infiltration should be implemented. Second, new materials, such as layered organic crystals (e.g., tetracyanoquinodimethane salts) or thin films - with built-in high electric fields and nanoengineered spaces sufficient for hydrogen molecules - should be investigated to capitalize on the same principle employed for the nanohorns.

## FY 2009 Publications/Presentations

1. “Single-Walled Carbon Nanohorns for Hydrogen Storage and Metal Catalyst Supports”, David B. Geohegan, Invited Presentation at Solid Storage of Hydrogen (SSH-IP) Workshop, Fodele, Greece, June 10, 2009.
2. “Hydrogen storage in charge compensated organic molecular crystals”, Mina Yoon and Matthias Scheffler, Contributed talk at American Physical Society March Meeting, Pittsburgh, Pennsylvania, March 18, 2009.
3. “First principles design of electric-field-assisted high capacity hydrogen storage media”, Mina Yoon, Invited talk at American Physical Society March Meeting, Pittsburgh, Pennsylvania, March 16, 2009.
4. “Interaction between hydrogen molecules and metallofullerenes”, M. Yoon, S. Yang, Z. Zhang, *J. Chem. Phys.* (2009).
5. “Electric field assisted hydrogen storage mechanism in charge transfer organic crystals” M. Yoon, M. Scheffler (in preparation).
6. “Calcium as a superior coating metal in functionalization of carbon fullerenes for high-capacity hydrogen storage”, M. Yoon, S. Yang, C. Hicke, E. Wang, D. Geohegan, Z. Zhang, *Phys. Rev. Lett.* **100**, 206806 (2008).
7. “Cumulative and continuous laser vaporization synthesis of single wall carbon nanotubes and nanohorns” A.A. Puretzky, D. Styers-Barnett, C.M. Rouleau, H. Hu, B. Zhao, I.N. Ivanov, D.B. Geohegan, *Appl. Phys. A* **93**, 849 (2008).
8. “Electron transfer and localization in endohedral metallofullerenes” Shenyuan Yang, Mina Yoon, Zhenyu Zhang, and Enge Wang, *Phys. Rev. B* **78**, 115435 (2008).
9. “Energetics and kinetics of Ti clustering on neutral and charged C-60 surfaces” Shenyuan Yang, Mina Yoon, Enge Wang, and Zhenyu Zhang, *J. Chem. Phys.* **129**, 134707 (2008).